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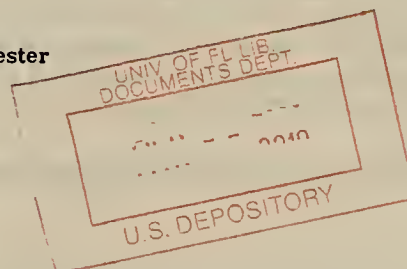
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A RAPID METHOD FOR THE DETERMINATION OF NITROGEN OXIDES IN AIR

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## A RAPID METHOD FOR THE DETERMINATION OF NITROGEN OXIDES IN AIR

By John F. Flagg and Ralph Lobene

### INTRODUCTION

There are available at present two distinctly different types of method for determining nitrogen oxides ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ) in air. The first of these<sup>1</sup> involves oxidation of the oxides to nitric acid using hydrogen peroxide, after first absorbing the gas from a definite volume of air in a suitable solution. The nitric acid is then determined by conventional means, such as the diphenylamine, chloranil, phenoldisulfonic acid, or polarographic methods.

The second method<sup>2</sup> involves absorption of the oxides in a suitable solution and determination of the nitrous acid produced. This is done by use of the alpha naphthyl amine-sulfanilic acid reagent.

The first method gave good results in the hands of the originators and would appear to suffer no defect save the fact that a two-hour oxidation period is necessary before the final analysis can be made. The methods of final analysis (diphenylamine, etc) are standard and accurate. The second method, while more rapid, is empirical. The colorimetric determination of the nitrous acid is made in the syringe with which the air sample was taken, making for greater speed. The accuracy claimed is satisfactory — of the order of 20 per cent.

The method presented here was devised for rapid, semiquantitative field work, using a minimum of equipment and reagents.

### PRINCIPLE OF THE METHOD

The adsorptive power of silica gel is well known, and it seemed likely that small amounts of nitrogen oxides could be concentrated upon silica for further testing. This proved to be practicable; when air samples of suitable size containing nitrogen dioxide were drawn over small amounts of silica in glass tubes, complete removal of the gas was noted. It remained then only to find a reagent with which the silica might be treated in order to develop a color with the adsorbed gas. Diphenylamine in sulfuric acid was found a satisfactory reagent for this purpose, developing a blue color the intensity of which is proportional to the amount of  $\text{NO}_2$  present. (In what follows we shall assume that we are dealing primarily with the oxide  $\text{NO}_2$ .)

The colors developed by treating the silica with diphenylamine reagent could be compared with known standards and thus the concentration of  $\text{NO}_2$  in the air-gas mixture determined. Another method was also tried in which the diphenylamine was added directly to the silica without removing it from the tube. The length of the colored zone was observed after the manner of chromatographic adsorption. The first method gave more satisfactory results.

### EXPERIMENTAL PART

#### Reagents

1. Silica: Silica gel, obtained from the Davidson Chemical Co., Baltimore, Maryland, was cleaned by heating about 50 cc with 100 cc of 6N HCl. Heating proceeded for 30 minutes; the acid was decanted, and the silica was washed hot with several hundred cc of distilled water. Iron is the

principal impurity removed by this process. The silica was then dried, ground, and sieved. The portions saved were 40-60\*, 60-80, 80-100, 100-150. These portions were dried at 150 to 180°C until no more steam was evolved (about 1 hour), then stored in tightly capped bottles. The material should be almost perfectly white after this treatment.

2. The nitrate standard was made by dissolving 72.16 mg of  $\text{KNO}_3$  in 100 ml of water. This solution contained 328 ppm of nitrogen as  $\text{NO}_2$ . This solution was diluted to secure standards of lower concentration.

3. Diphenylamine reagent was prepared by dissolving 50 mg of diphenylamine in 25 ml of concentrated  $\text{H}_2\text{SO}_4$ .

4. Nitrogen dioxide was prepared before each series of experiments by treating copper with concentrated nitric acid.

#### Apparatus

The only apparatus used consisted of (1) a 50-cc Yale B-D syringe for taking samples, (2) 1- and 5-liter flasks for storing the air-gas mixtures, and (3) numerous glass tubes, 4-mm inside diameter, about 40 mm long, in which the silica was placed.

#### Method

1. Synthetic samples: The method of preparing atmospheres containing known amounts of  $\text{NO}_2$  was as follows. Nitrogen dioxide was generated by the action of nitric acid on copper in an evacuated flask. When the pressure of the gas was slightly greater than atmospheric, a sample was collected in an evacuated pipet. Several pipets were used, with capacities of 2 to 5 cc. After equalizing the pressure of the sample with the atmosphere, the  $\text{NO}_2$  was washed with air into either a 1- or 5-liter flask. The mixture was thoroughly mixed by pumping with the syringe. Using the temperature and barometric pressure, the volume of  $\text{NO}_2$  at NTP could be calculated and thus the parts per million in the synthetic mixture. If the concentration of a given mixture was too high, 50-cc samples of it were diluted again in the manner described.

2. Taking the samples: A glass tube filled with 20 mm of silica (100-150) and plugged at each end with glass wool was attached by means of rubber tubing to the syringe. A 50-cc sample was drawn in slowly, then slowly expelled. The silica was then ready for treatment with diphenylamine.

3. Development of color: One plug of glass wool was removed from the tube and the silica poured into a depression on a spot plate. In adjacent spots similar amounts of fresh silica were placed. Two drops of the various nitrate standards were placed on the fresh silica. Then to both standards and unknown were added 12 drops of diphenylamine reagent. After 4 to 5 minutes, stirring meanwhile, the colors were compared. Determinations were usually made in triplicate, and a blank run on the silica itself.

#### RESULTS

The conditions finally chosen for making the analyses consisted in taking a 50-cc air-gas sample and comparing it with the nitrate standards as described before. Figure 1 shows the results of these comparisons. The relationship between ppm in the gas and in the solution is linear over the useful range. When the gas concentration is over 50 to 60 ppm, the color produced from a 50-cc sample is too intense for accurate comparison with the standards. Presumably a smaller sample (25 cc) could be taken, although this was not tested carefully. With concentrations of 1 to 5 ppm, the color produced with a 50-cc sample is faint, though easy to match. With smaller concentrations, a 100-cc sample might be taken.

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\* Passed the 40 mesh sieve, not the 60, etc.



Inasmuch as the nitrate standards can be read to only 3 ppm, it is seen from the curve that the concentration of the gas can be read only to  $\pm 5$  ppm. Thus the accuracy of the method is limited, although at lower concentrations the error is probably somewhat less.

A reasonably good check may be obtained, upon calculation, between the amount of  $\text{NO}_2$  on the silica and in the nitrate standard. Consider the gas concentration at 20 ppm. From Figure 1 it is seen to match the nitrate standard having 10 ppm. In the 50-cc gas sample there was present  $50/1000 \times .04 \text{ mg} = 0.002 \text{ mg}$  of  $\text{NO}_2$ . (20 ppm of  $\text{NO}_2$  is .04 mg/liter.) The nitrate standard contained 3 grams of N, or about 10 grams of  $\text{NO}_2$ , per million grams of water. Since, however, only 2 drops of this solution were used for the test, the total amount of  $\text{NO}_2$  on the spot plate was  $.1/10^6 \times 10 \text{ g} = 10^{-6} \text{ gram}$ , or 0.001 mg of  $\text{NO}_2$ . Thus, the nitrate solution is about twice as efficient in producing a color as the adsorbed gas. The explanation for this probably lies in the findings of Patty and Patty,<sup>2</sup> who found that  $\text{NO}_2$ , when treated with water, is converted only to the extent of 57% into  $\text{HNO}_3$ .

#### CHARACTERISTICS OF THE ADSORPTION PROCESS

**Mesh Size of the Silica:** The larger mesh sizes (40-60, 60-80, 80-100) work well, and offer little resistance to drawing the sample. The color produced upon development is difficult to compare with the standards, since it is the particles themselves that are colored. The color is more uniform with small mesh sizes (100-150). Particles smaller than these offer considerable resistance to drawing and are not satisfactory.

**Depth of Silica Layer:** Using a 4-mm (inner diameter) tube, 10 mm of silica will remove 10 or 20 ppm of  $\text{NO}_2$  from a 50-cc sample; 20 mm of silica will remove up to 100 ppm from a 50-cc sample. Use of deeper beds of silica offers no advantage and only makes comparison difficult later.

**Retention of the Gas:** Tubes containing adsorbed  $\text{NO}_2$ , from a 20-ppm sample, showed no loss of gas after one week.

**Interfering Substances:** Presumably other oxidizing gases such as ozone would interfere. No tests have been made.

**Sample Sizes:** There is a direct proportionality between sample size and color developed. For example, if a 10-cc sample of gas gives a color matching 1 ppm nitrate standard, then a 20-cc sample will match 2 ppm nitrate standard, etc.

**"Chromatographic" Adsorption:** In a number of cases, diphenylamine was added directly to the silica tube after adsorption of the gas. The depth of the colored zone was observed and an attempt made to correlate zone depth with concentration. Zone depth was influenced too much by washing and time of standing to be a reliable indicator of concentration.

#### SUMMARY

1. A method has been devised for adsorbing  $\text{NO}_2$  on silica gel, treating with diphenylamine, and comparing the color with standards.

2. The method is applicable to air-gas mixtures containing from 1 to 50 ppm of  $\text{NO}_2$ .

3. Advantages claimed are sensitivity and speed; only simple apparatus and reagents bring required. Disadvantage lies in only moderate accuracy.

#### REFERENCES

1. Cholak and McNary, J. Ind. Hygiene and Toxicology, 25, 351 (1943)
2. Patty and Patty, *ibid*, 25, 361 (1943).

